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(71)Applicant : NGK INSULATORS LTD

(72)Inventor : NODA NAOMI
SUZUKI JUNICHI
TAKAGI SHIGEKAZU

(54) CARRIER CARRYING ALUMINA, CATALYST BODY AND METHOD FOR MANUFACTURING CARRIER CARRYING ALUMINA

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a carrier in which a catalyst body hardly causing deterioration of the carrier by alkali metals or alkaline earth metals even for long-term use can be manufactured even when the carrier carries alkali metals or alkaline earth metals, particularly a catalyst material comprising Li, Na, K and Ca, typically a NOx occlusion catalyst as a catalyst material for cleaning exhaust gas from an automobile, and to provide a method for manufacturing the carrier, and to provide a catalyst body comprising the carrier carrying the catalyst material.

SOLUTION: In the carrier having a specified structure, alumina, and if desired, a substance which easily reacts with alkali metals and/or alkaline earth metals to be used as the catalyst component, and/or alkali metals and/or alkaline earth metals are disposed in the carrier and/or on the surface of the cell wall of the carrier.

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CLAIMS

[Claim(s)]
[Claim 1] Support which is the support which consists of a kind of structure chosen from the group which consists of a monolith honeycomb, a pellet, a bead, a ring, and form, and is characterized by coming to arrange an alumina on the inside of said support, and/or the cell wall front face of said support.
[Claim 2] Support according to claim 1 which comes to arrange the alkali metal and/or alkaline earth metal which are further used for the inside of said support, and/or the cell wall front face of said support as a catalyst intermediation component, the matter which is easy to react, alkali metal, and/or alkaline earth metal.
[Claim 3] Support according to claim 2 said alkali metal and/or alkaline earth metal, and whose matter which is easy to react are silicas.
[Claim 4] Support according to claim 2 or 3 which is that by which said silica is directly arranged on said support, and the alumina is arranged on it.
[Claim 5] Support given in any 1 term of claims 1-4 said whose support is honeycomb objects.
[Claim 6] Support given in any 1 term of claims 1-5 in which said support contains cordierite as a principal component.
[Claim 7] Support given in any 1 term of claims 1-6 which are the things containing at least one sort chosen from the group which said alumina becomes from gamma-alumina, delta alumina, eta alumina, theta alumina, alpha-alumina, and an amorphous alumina.
[Claim 8] Support according to claim 7 said whose alumina is what contains alpha-alumina as a principal component.
[Claim 9] The catalyst object which supports catalyst material to support given in any 1 term of claims 1-8.
[Claim 10] The catalyst object according to claim 9 which is that in which catalyst material contains alkali metal and/or alkaline earth metal.
[Claim 11] The manufacture approach of support that the alumina characterized by calcinating the support which obtained the support with which support was made to support an alumina and the primary alumina was supported, and was subsequently obtained once [at least] was supported.
[Claim 12] The manufacture approach of support that the alumina according to claim 11 which calcinates the support with which said primary alumina was supported once [at least] after desiccation processing was supported.
[Claim 13] The manufacture approach of support that the alumina according to claim 11 or 12 which calcinates the support with which said primary alumina was supported once [at least] at the temperature of 200 degrees C or more was supported.
[Claim 14] The manufacture approach of support that the alumina of a publication was supported by any 1 term of claims 11-13 which calcinate the support with which said primary alumina was supported once [at least] at the temperature of 1300 degrees C or less.
[Claim 15] The manufacture approach of support that the alumina of a publication was supported by any 1 term of claims 11-14 which use the gap or one sort of ingredients which be chosen as support of said alumina from the combination of alumina powder, alumina sol, or alumina powder and alumina sol.
[Claim 16] The manufacture approach of support that the alumina of a publication was supported by any 1 term of claims 11-13 which use alumina sol for support of said alumina.
[Claim 17] The manufacture approach of support that the alumina of a publication was supported by any 1 term of claims 11-16 including the process which makes the alkali metal and/or alkaline earth metal which are used as a catalyst component, the matter which is easy to react, alkali metal, and/or alkaline earth metal support.

[Claim 18] The manufacture approach of support that the alumina according to claim 17 which uses the sol of the alkali metal and/or alkaline earth metal which are used for support of the alkali metal and/or alkaline earth metal which are used as said catalyst component, the matter which is easy to react, alkali metal, and/or alkaline earth metal as said catalyst component, the matter which is easy to react, alkali metal, and/or alkaline earth metal was supported.
[Claim 19] The manufacture approach of support that the alumina according to claim 17 or 18 whose sol of the alkali metal and/or alkaline earth metal which are used as said catalyst component, the matter which is easy to react, alkali metal, and/or alkaline earth metal is a silica sol was supported.
[Claim 20] The manufacture approach of support that the alumina of a publication was supported by any 1 term of claims 11-13 which perform said baking twice.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the manufacture approach of alumina support support and this support support, and a catalyst object. Alkali metal and alkaline earth metal which are represented as catalyst material in more detail by the NOx occlusion catalyst for automobile exhaust clarification, It is the support used since the catalyst material which contained Li, Na, K, and calcium especially is carried. the catalyst which degradation does not generate substantially even if degradation of the support by alkali metal or alkaline earth metal is inhibited, it carries catalyst material and it uses it over a long period of time -- support usable as the body and its function -- It is related with the catalyst object which supported the manufacture approach of this support, the alkali metal represented by this support for a NOx occlusion catalyst at a list and alkaline earth metal, the catalyst material that contained Li, Na, K, and calcium especially.
[0002]
[Description of the Prior Art] While emission control was tightened up in recent years, the lean burn engine, the direct-injection engine, etc. followed on spreading, and the NOx occlusion catalyst which can purify NOx in exhaust gas effectively under lean atmosphere was put in practical use. As a NOx occlusion component used for a NOx occlusion catalyst, rare earth, such as alkaline earth metal, such as alkali metal, such as K, Na, Li, and Cs, and Ba, calcium, and La, Y, etc. is known, and especially Ba is used more widely than the time of utilization of a NOx occlusion catalyst. Moreover, recently, addition of K which is excellent in the NOx occlusion ability in a high temperature region is being tried.
[0003]
[Problem(s) to be Solved by the Invention] By the way, although a NOx occlusion catalyst usually support the catalyst material containing said NOx occlusion component to the support which consist of an oxide system ceramic ingredient like cordierite, or a metallic material like a Fe-Cr-aluminum alloy and be constitute, it be corrode by the alkali metal which became activity under the elevated temperature of exhaust gas, some alkaline earth metal, division, and Li, Na, K and calcium, and such support have the problem of be easy to deteriorate. In the case of the cordierite support which consists of oxide system ceramic ingredients especially, it reacts with the above-mentioned alkali metal etc., a crack occurs in it, and it has been a serious problem.
[0004] In addition, although the activated alumina is used for the catalyst object for emission gas purification from the former as a support base material which has the high specific surface area for carrying out high distribution of the catalytic activity component represented by noble metals etc. In the catalyst object which comes to support the catalyst material containing alkali metal and/or alkaline earth metal with this invention to support By giving precoat of an alumina to the support before catalyst support, it differs in that it is the object which protects the support represented by the cordierite honeycomb from a reaction with the contact to the alkali metal in a catalyst bed, and/or alkaline earth metal, as a result that, etc.
[0005] The place which this invention is made in view of such a conventional problem, and is made into the object Are suitable support to support the catalyst material containing the alkali metal and alkaline earth metal like a NOx occlusion catalyst, and when it is used as a catalyst object, degradation suppression of the support according to alkali metal or alkaline earth metal is possible. And it is in offering the manufacture approach of the possible support of a long-term activity, and this support, and the catalyst object which made this support support catalyst material.
[0006]
[Means for Solving the Problem] According to this invention, in suitable support to support the catalyst

material containing alkali metal and/or alkaline earth metal, the support characterized by coming to arrange an alumina on the inside of support and/or the cell wall front face of support and the catalyst object which made this support support catalyst material are offered.
[0007] Moreover, the manufacture approach of support that the alumina characterized by calcinating the support support obtained in this way including the process which makes support support the process which makes support support an alumina, the alkali metal and/or alkaline earth metal which use as a catalyst component by request, the matter which is easy to react, alkali metal, and/or alkaline earth metal according to this invention was supported is offered.
[0008]
[Embodiment of the Invention] In this invention, the reactant low alumina is beforehand arranged on the inside of support, and/or the cell wall front face of support to the alkali metal and/or alkaline earth metal which are used as catalyst material. Thus, even if it is exposed to an elevated temperature while the catalyst object which made catalyst material support uses it by Lycium chinense, since it is protected from alkali metal and/or alkaline earth metal by the alumina and a reaction with these is suppressed with it, as for support, degradation is inhibited as a result.
[0009] Although various phases are known, in this invention, stability is important for an alumina and gamma-alumina, delta alumina, eta alumina, theta alumina, alpha-alumina, an amorphous alumina, etc. are suitable for it. Generally, it can be preferably said in that alpha-alumina is the point of high corrosion resistance, it is desirable, and an amorphous alumina tends to form a precise protective coat depending on an operating environment that it is desirable with the point that the familiarity of gamma-alumina by catalyst material is good. However, it can be said that it is a surprising thing that the effectiveness considered as a request is demonstrated, without being substantially influenced by the class of alumina phase, if the alumina layer of the thickness considered as a request is formed anyway.
[0010] In addition, each phase of an alumina may be used independently, and may mix two or more phases, and may be arranged. For example, making the special feature of alpha phase or gamma phase discover by carrying out mixed arrangement of alpha phase, amorphousness and gamma phase, and the amorphous substance, amorphous compactness can be made to have and it is desirable.
[0011] the gestalt of the alumina when supporting (arrangement) -- especially -- a limit -- there is nothing -- an alumina -- although it may be independent or you may be a composite with other matter, and mixture, the alumina from a corrosion resistance viewpoint is more than 90 mass % -- if it puts in another way, it is still more nearly substantially desirable alumina independence and to arrange only an alumina. When compounding and/or mixing other components, it is desirable to choose what has the operation which raises a corrosion resistance high thing, the corrosion resistance of an alumina, and thermal resistance to alkali metal and/or alkaline earth metal in itself.
[0012] in addition -- as the source of an alumina -- alumina powder -- only alumina powder and alumina sol are more preferably used [alumina sol] for alumina powder and alumina sol substantially still more preferably. In addition, as a source of an alumina, by using only alumina sol substantially, since support can be coated with a precise alumina, it is desirable. Moreover, by coating alumina sol and alumina powder, since there is also no crack initiation in the surface part of alumina coating which can adopt a higher burning temperature and is formed as compared with the case of alumina sol independent coating and the alumina of the specified quantity can be coated with the further more small count of coating, it is desirable. The class of alumina to be used, the support approach, and baking conditions are explained in full detail below.
[0013] In supporting with relation with the support approach, using a solid-state (powder) as a concrete source of an alumina In supporting using a liquid (a solution or dispersion liquid), an oxide etc. The thing of a gestalt to which various solutions or dispersion liquid (it is hereafter named generically "the source content liquid of an alumina"), such as a nitrate, a sulfate, a hydroxide, a chloride, an organic-acid salt, and alumina sol, is suitably used, and no components other than an alumina remain to the catalyst inside of the body by processing of baking etc. especially is desirable. The following approaches can be mentioned as an approach of arranging an alumina between support and the catalyst material in support.
[0014] [the approach of arranging an alumina in support] -- by immersing support in the viscous low source content liquid of an alumina comparatively, the interior of the so-called virgin support in which coating is carried out and this liquid is not with a catalyst etc. can be made to be able to permeate, and the source of an alumina can be arranged in this support. This approach is suitably used, when support is porosity, and it can introduce the source of an alumina even on the surface of an open pore. Moreover, you may be the technique of adding the source of an alumina in the raw material in the phase (production process) which produces support. In this case, it may add in the form of a solution or dispersion liquid, or the source of an

alumina may be added in the form of solid-states (powder) including an oxide. Although the added source of an alumina may form other raw materials and a compound in the production process of support, to exist as an alumina is more desirable. From a viewpoint which controls contact to exposure of support material, i.e., the alkali metal in catalyst material, and/or alkaline earth metal by the technique immersed in the source content liquid of an alumina in support, and the technique of adding the source of an alumina in the support raw material, the former immersion technique is more desirable. Although using the construction material of support itself as an alumina may naturally raise corrosion resistance most, it is required at the time of an activity to limit to carry out temperature control and an application etc. in this case so that the low thermal shock resistance of an alumina may not pose a problem.

[0015] It is rare to be influenced especially according to the structure of support in the [approach of arranging precoat layer containing alumina on cell wall front face of support] support unlike the case where an alumina is arranged. As concrete technique, an alumina can be comparatively arranged as a precoat layer between the layers which consist of catalyst material which demonstrates the effectiveness of support and a request by coating support with this liquid using the viscous high solution or dispersion liquid containing alumina sol etc. As a source of an alumina, when alumina sol is used for a pan more than 90 mass % more than the whole 50 mass % by solid content, it is desirable at the point of being easy to form a precise precoat layer. It is much more desirable to use only alumina sol substantially.

[0016] As other examples, by, for example, slurring and coating alumina powder etc., this precoat layer may be arranged and the technique of adding an organic binder and/or an inorganic binder is also still more desirable at the point that a precoat layer stops being able to exfoliate easily, in the case of slurrying. Alumina sol is the most desirable at the point of the alumina rate in a precoat layer increasing especially, and contributing also to eburnation. When using alumina powder, the thing of various phases is used suitably as mentioned above. Moreover, two or more sorts from which a phase, particle size, a presentation, etc. differ may be mixed and used, and order may be coated later on independently. In addition, in the technique of arranging these precoat layers, although a part of solution or dispersion liquid, and slurry may invade in support through an open pore etc. in the case of coating when support is porosity, there is especially no problem.

[0017] In the above, although divided and explained, both of followings decide to explain the matter common to law of the approach of arranging an alumina in support, and the approach of arranging the precoat layer containing an alumina on the cell wall front face of support collectively.

[0018] It is also one of the desirable embodiments to coat alumina powder and alumina sol by turns. Under the present circumstances, first, alumina powder is coated, and if alumina sol is coated, the front face of coating can be made more precise, reverse is first coated with alumina sol, and subsequently, if alumina powder is coated, the adhesion to support can be raised more. Even if it is which order, alumina sol may be further used simultaneously as an inorganic binder in coating of alumina powder. When carrying out sequential coating of it etc. using two or more sorts of different sources of an alumina, such as a gestalt, particle size, a phase, a presentation, and concentration, it is desirable to coat sequentially from a kind with a large particle size from a viewpoint of the membrane formation nature on the front face of the maximum.

[0019] When using alumina sol, 2Oaluminum3 content in a sol has desirable 3 - 30 mass %. It is because inconvenience, such as becoming easy to generate blinding at the time of coating, may occur according to viscous buildup if under 3 mass % causes buildup of the count of coating and 30 mass % is exceeded. Furthermore, 5 - 25 mass % is more desirable.

[0020] When using alumina sol, although acids, such as HCl, HNO3, and CH3C OOH, are desirable, the inorganic acid of the pH stabilizer is more more desirable, and its HNO3 is dramatically more desirable than an organic acid especially. in addition, the magnitude of the particle (colloid) which constitutes alumina sol in that case may invade to the micropore, when support is the porosity of the honeycomb structure object made from a ceramic etc. -- as -- the colloid mean particle diameter of alumina sol -- the average pore size >= colloid mean particle diameter of support -- it chooses so that it may consider as the average pore size x10%>= colloid mean particle diameter of support preferably. Specifically, it is desirable to be referred to as 500nm or less with colloid mean particle diameter. If it is 200nm or less, a carrier surface can be precisely covered after baking, it is more desirable, and 100nm or less is still more desirable.

[0021] When using alumina powder, when support is porosity, as for the particle size, it is desirable the appearance which may invade to the micropore, the average pore size >= alumina powder mean particle diameter of support, and to consider as the average pore size x30%>= alumina powder mean particle diameter of support further. It is desirable that the mean particle diameter of alumina powder is 1 micrometer or less, and if it is 0.5 micrometers or less, specifically, it is still more desirable.

[0022] When mixing and using alumina powder and alumina sol, the suitable mixing ratio is aluminum2O3 minute =1:0.2-1:4 among alumina powder:alumina sol. If the effectiveness which originates in the used alumina powder if alumina powder is mixed so that it may become 1:4 or more about alumina powder can be made to discover suitably and alumina sol is mixed or more to 1:0.2 on the other hand with both mixing ratio, the compactness originating in alumina sol can be made to discover suitably. Both mixing ratio is 1:0.5-1:2 still more preferably. Both merits can be made to discover with sufficient balance within the limits of this.
[0023] Other corrosion resistance, such as a mullite, a zirconia, a titania, and SiC, or besides alumina powder, it mixes with the source content liquid of an alumina including alumina sol, and desirable technique also uses the powder of an excellent ingredient for coating.
[0024] When coating of multiple times is performed using the coat material of the same coat material or a different gestalt, a phase, particle size, a presentation, and concentration, What could perform desiccation and baking after each coating, and was coated previously At the time of the next coating, even if it is not calcinating, as long as the re-eluted concern is small, it may collect at the end and you may calcinate, but when previous coating is completed also in such a case, drying at least is desirable. When collecting at the end and calcinating, while a process can be simplified, in performing desiccation -> baking after each coating, it becomes possible to set up mutually different baking conditions according to each coat material. Moreover, if the concern in which what already carried out precoat is re-eluted in continuing catalyst coating is small, precoat can also be ended only by desiccation. In this case, baking after catalyst material support will serve as baking after alumina support, and a process is simplified. Although the quick drying by the box mold dryer or hot air drying equipment is simple and efficient and is applied suitably, desiccation can improve by air drying, gas conditioning desiccation, freeze-drying, etc., when the crack on the front face of a coat poses a problem.
[0025] After carrying out coating like ****, you may calcinate without making it make dry or dry. Of course, after carrying out multiple-times coating of the coat material or the coat material which is different from each other of the same class, you may calcinate and may calcinate after each coating. When carrying out multiple-times coating, coat material which is different from each other, such as a component, a gestalt, a phase, and particle size, may be used by turns. In addition, when carrying out multiple-times coating, it may calcinate for every coating and the process of coating -> baking may be repeated. In this case, the coat material which may use the same coat material before and after the first baking, and is different from each other in either, such as a component, a gestalt, a phase, and particle size, before and after the first baking may be used. When calcinating twice, the 1st time and 2nd baking may be performed on the same conditions, and the 1st time and 2nd baking may be performed on different conditions.
[0026] It is also desirable technique to use together alkali metal, the component which is easy to react and the alkali metal mentioned later, and/or alkaline earth metal, and to apply combining "arrangement in support" and "interlayer arrangement" if needed further, using two or more sources of an alumina or sources of an alumina which have a different gestalt, a phase, particle size, a presentation, concentration, etc.
[0027] When support is porosity, it is desirable to reduce water absorption to 20% or less and 10 more% or less by coating. After coating of an alumina, in case the catalyst material slurry containing alkali metal is supported, it is because osmosis in the interior of support of this slurry can be controlled.
[0028] Although the approach (it arranges) of supporting an alumina on the inside of support and/or the cell wall front face of support is not restricted to these, in any case, it is once calcinated at the temperature of 250 degrees C or more in the phase which supported the alumina, and fixes an alumina in it. In order to make catalyst material support, it is desirable to prepare on an alumina the layer which consists of NOx occlusion catalyst material containing the catalyst material which demonstrates the effectiveness considered as a request, for example, alkali metal, and alkaline earth metal. If it considers as 500 degrees C or more, it is much more certainly fixed. When supporting an alumina and sources of an alumina other than the alumina itself are used, it is desirable that the used source of an alumina calcinates at the temperature beyond dehydration or the temperature which decomposes or oxidizes and generates an alumina. In coating the coat material which contains alumina sol especially, in order that alumina sol may solidify at 80-150 degrees C, you may make it fix only by 80-250-degree C desiccation. In this case, a process not only becomes simple, but it can control that a crack goes into the front face of coating with heat.
[0029] Furthermore, it is possible by controlling burning temperature to also make a desired alumina phase discover. For example, although alpha-alumina powder can also be coated as a raw material to obtain corrosion resistance high alpha phase, after supporting using another sources of an alumina, such as alumina powder of other phases, such as gamma-alumina, or alumina sol, desirable technique also promotes

pregelatinization at the point of making precise alpha-alumina phase form by calcinating at the temperature of 1000 degrees C or more in an atmospheric-air ambient atmosphere. Furthermore, if 1100 degrees C or more, since pregelatinization will be accelerated, it is still more desirable. It is also a suitable gestalt that all have alpha phase after baking. On the contrary, calcinating below 900 degrees C is desirable to obtain gamma phase. Although it faces manufacturing a catalyst object continuously and the alumina phase control by burning temperature is possible also in the baking process after catalyst material support, it is necessary to stop the temperature which can be set up in the range in which catalyst material does not deteriorate.
[0030] Support of an alumina is good in a multiple-times line if needed, as already stated. in that case, a desiccation process -- between -- being ****** -- only ****** and coating may be repeated two or more times, and you may calcinate at the end, and may calcinate also not only between the last but between the impregnation of multiple times, or coating. In that case, not to mention coat material, for example, the class of source of an alumina, a property, etc., even if the support approach, desiccation / baking conditions, etc. are the same, they may change with times. For example, in the 1st support, at least 1000 degrees C or more are preferably calcinated at the temperature of 1100 degrees C or more after the impregnation of the source of an alumina, or coating. Precise alpha phase can be made to be able to generate, gamma phase can be made to be able to generate in the 2nd continuing support by calcinating at the temperature of 900 degrees C or less after the impregnation of the source of an alumina, or coating, and it can mention as a suitable example making familiarity by the catalyst material further supported on it improve. If an amorphous substance is made intermingled in gamma-alpha each phase, a front face can be made to also have compactness in addition to the special feature of each phase.
[0031] Also when especially a limit does not have the configuration of the support used for this invention and support of which configuration, such as a monolith honeycomb, a pellet, a bead, a ring, and form, is used, the above degradation suppression effectiveness is acquired, but effectiveness is the largest when the support (honeycomb support) of the honeycomb configuration which consists of breakthroughs (cel) of a large number divided with the septum thin especially is used.
[0032] By the way, when using it as support which uses alkali metal as a catalyst, in order that using combining the alkali metal currently indicated by the JP,2000-279810,A official report and the component which is easy to react may also heighten the degradation depressor effect of support further as a whole, it is desirable. For example, when combining with alkali metal and the silica which is the component which is easy to react, and the coat of the silica was turned up first and the coat of the alumina was carried out in piles, after defending to diffusion of K from a catalyst bed with the alumina which is anticorrosion material first, about K which leaks to a support side further, the two-step style of different operation of carrying out a trap by the silica eventually can be presented.
[0033] Moreover, it is desirable in order that using for the application for patent 2001-213258 of application on July 13, Heisei 13 concerning an invention-in-this-application person's etc. invention combining at least one sort of alkali metal and/or alkaline earth metal based on the approach of a publication may similarly heighten the degradation depressor effect of support further as a whole. When combining with the barium oxide containing the potassium silicate (K_2SiO_3) containing alkali metal, or an alkaline earth metal, the coat of the potassium silicate can be carried out in piles on an alumina, or the coat of the alumina can be carried out in piles on the barium oxide at reverse, and the two-step style of a different operation can be presented. Or an alumina raw material can also be used for one sort of alkali metal and/or alkaline earth metal, and coincidence, even if there is none of these **. Therefore, the publication of an application for patent 2001-213258 is quoted by reference here.
[0034] A more desirable result is obtained when combining with the alkali metal and/or alkaline earth metal which are used as catalyst components, such as this, the matter which is easy to react, alkali metal, and/or alkaline earth metal, and all also of coat material, such as silicas other than an alumina, use only a sol as a raw material substantially.
[0035] Thus, in carrying out the coat of two or more components which have a different operation, the direction which separates and carries out a coat to stratified ** tends to discover each operation effectively, but in the case of two or more components which show the same operation, of course, even if it mixes and carries out a coat, it does not interfere.
[0036] Although the quality of a ceramic, the quality of metal, etc. are not restricted since this invention is applied to various support components and the effectiveness is discovered, for example with SiC of the cordierite of an oxide system ceramic ingredient, a mullite, an alumina, a zirconia, a titania, a spinel, phosphoric-acid zirconyl, aluminum titanate, germanium-cordierite, and a non-oxide system ceramic ingredient, SiN, and a metal ingredient, a Fe-Cr-aluminum alloy etc. can apply especially the ingredient of

support suitably. When using the oxide system ceramic support which is easy to receive the corrosion by alkali metal or alkaline earth metal especially, effectiveness is large and it is dramatically effective to the cordierite support currently used widely in the field of the catalyst for automobile exhaust clarification. Moreover, cordierite is suitably applicable also to what is included 10% or more as the support which consists of support which consists of the mixed stock of two or more sorts of ingredients, and a multicomputer system, for example, the ingredient which combined the mullite particle and the SiC particle by cordierite, especially a component.

[0037] The breakthrough configurations (cel configuration) of honeycomb support may be which configurations, such as circular, a polygon, and a corrugated mold. Moreover, the appearance of honeycomb support should be formed in the predetermined configuration of having been suitable for the inner configuration of the exhaust air system to install.

[0038] Although especially a limit does not have the cel consistency of honeycomb support, either, it is desirable as catalyst support that it is the cel consistency of the range of 6-1500 cel / square inch (0.9 - 233 cel / cm2). Moreover, the thickness of a septum has the desirable range of 20-2000 micrometers. In the case of a 20-200-micrometer thin wall, since diffusion of alkali metal and/or alkaline earth metal is easy from catalyst material to the core of support wall thickness, the need for this invention increases and the degradation suppression effectiveness also increases.

[0039] Especially a limit does not have the porosity of honeycomb support, and in the case of 10% or more and 20 more% or more of high porosity, since diffusion of alkali metal and/or alkaline earth metal becomes easy through an open pore, the need for this invention increases and the degradation suppression effectiveness also increases. In addition, as for the coefficient of thermal expansion of the support after coating, it is desirable that it is less than [8.0x10-6/degree C] from a viewpoint of thermal shock resistance required of motor exhaust. Less than [4.0x10-6/degree C] is still more desirable, and if it is less than [2.0x10-6/degree C], loading will become possible also in the location near an engine.

[0040] The amount of the alumina arranged to support has desirable 0.5 - 200 g/L per catalyst object unit volume at conversion. When the support degradation suppression effectiveness is small when it is less than 0.5 g/L, it supports to the same support as a NOx occlusion catalyst exceeding 200 g/L, and honeycomb support is used, the blinding of a cel may arise. Preferably, it is the range of 30 - 80 g/L still more preferably ten to 100 g/L. Especially, from the point of balance with prevention of crack initiation and lowering control of anti-chip box reinforcement, and pressure loss, it is desirable that it is the range of 40 - 70 g/L. In addition, it cannot be overemphasized that the amount of the alumina used for the amount of this alumina as a support base material which has the high specific surface area for carrying out high distribution of the catalytic activity component represented by the noble metals used according to the application of a catalyst object is not included.

[0041] The alumina layer formed on support is 10 micrometers or less preferably 20 micrometers or less, when one side of a septum is measured near the center of one side of cels to the shaft orientations of support, using an electron microscope as thickness after baking in a vertical cross section. If it exceeds 20 micrometers, since pressure loss will increase, it is not desirable.

[0042] The viscosity of the coat liquid represented by alumina sol is below 30mPa(s).s still more preferably below 500mPa(s).s preferably below usual 10000mPa.s. Coating may become difficult, when viscosity exceeds 10000mPa(s).s and support is a honeycomb object. Moreover, in exceeding 500mPa.s, since blinding may be started depending on the support to be used, it requires caution. If it is below 30mPa(s).s, since the alumina layer moderate also in the pore of support which it permeated, was precise and was stuck is formed, it is desirable.

[0043] pH of alumina sol -- usually -- 2.0-6.0 -- it is 3.0-5.0 preferably. If pH is lower than 2.0, when support is not acid-proof construction material, since it may corrode by being immersed in coat liquid, it is not desirable. If 6.0 is exceeded, the particle in a sol may condense.

[0044] If it is within the limits which does not spoil an operation of the alumina concerning this invention, it will not interfere, even if other metals and/or a metallic oxide, carbide, a nitride, etc. are contained in the alumina. However, as for an alumina, not containing is [the noble metals for other catalysts etc.] desirable in respect of high temperature oxidation stability. Furthermore, in order to protect support from alkali metal, alkaline earth metal, etc. effectively, it is more desirable to be formed as support, the catalyst bed which contains alkali metal and/or alkaline earth metal at least, and a layer with an alumina independent in between. As long as it puts in another way, between the catalyst beds containing support, alkali metal, and/or alkaline earth metal, only the alumina layer may be formed intrinsically, and the laminating may be carried out on the layer which consists of other compound layer or other components with a component,

and/or to the bottom so that it may mention later. Of course, it cannot be overemphasized that it faces considering as a catalyst object and noble metals for burning in catalysts other than the so-called NOx catalyst, for example, a hydrocarbon etc., such as Pt, Pd, and Rh, may be contained in the catalyst bed to form. Moreover, making the catalyst bed containing noble metals, such as Pt, Pd, and Rh, form separately on a NOx catalyst bed is not restricted at all.
[0045] The catalyst object of this invention is also simultaneously [with other clarification material applied to an exhaust gas system, such as co-catalyst material, HC adsorption material, etc. which are represented by the oxide of the NOx occlusion catalyst material which consists of another constituent, the catalyst material of the another kind represented by the three way component catalyst, Ce and/or Zr,] applicable. In that case, although these may be made intermingled in the catalyst material of the catalyst object of this invention, the direction supported in piles in the shape of a layer is desirable at the point that thermal resistance increases more. Moreover, it can separate into a part for the catalyst object top of a piece object / downstream, and can also support. Furthermore, it may combine with these which were prepared as a separate object suitably within an exhaust air system, and you may use.
[0046]
[Example] Hereafter, although this invention is explained still more concretely based on an example, this invention does not receive a limit at all according to these examples.
[0047] [Preparation of the slurry for alumina support]
The slurry A for alumina support: The slurry A for alumina support was prepared by adding 2Oaluminum3 commercial sol and commercial moisture to 2Ogamma-aluminum 3 commercial powder (specific surface area: 200m2/g), and carrying out wet grinding to it with a pot mill. The addition of 2Oaluminum3 sol was made into the amount from which the solid content (2Oaluminum3 weight contained in 2Oaluminum3 sol) is 2Oaluminum3 conversion, and becomes 50 mass % of all aluminum 2O3, and it was suitably added so that it might become the viscosity which a slurry tends to coat about moisture.
[0048] The slurry B for alumina support: The slurry B1 for alumina support, B-2, and B3 were obtained like the slurry A for alumina support except 1:1, 1:0.1, and 1:0.3 having prepared three kinds of ratios of 2Oaluminum3 amount in having used 2Oalpha-aluminum 3 powder instead of and alpha alumina powder, and aluminum2O3 sol. [2Ogamma-aluminum 3 commercial powder]
[0049] Slurry B4 for alumina support: Slurry B4 for alumina support was obtained like the slurry A for alumina support except having added the organic binder (Toagosei acrylic Aron AS- 7503) of 10 mass %, and a suitable quantity of water by outside ** to 2Oalpha-aluminum 3 commercial powder.
[0050] The slurry C for alumina support: The slurry C for alumina support as well as the slurry A for alumina support was obtained except having set the mixture of 1:1 of having used the mixture of 1:1 of 2Oalpha-aluminum 3 powder and mullite powder instead of and 2Oalpha-aluminum 3 powder, and mullite powder, and the ratio of 2Oaluminum3 amount in aluminum2O3 sol to 1:1. [2Ogamma-aluminum 3 commercial powder]
[0051] After being immersed in the solution which mixed 2(NH3) Pt(NO2)2 water solution and KNO3 water solution and stirring gamma-aluminum 2O3 powder (specific surface area: 200m2/g) of [preparation of slurry for NOx occlusion catalyst coatings] marketing with a pot mill for 2 hours, evaporation to dryness of the moisture was carried out, the dry type crack was carried out, and it calcinated with the electric furnace at 600 degrees C for 3 hours. In this way, the slurry for coatings was prepared by adding 2Oaluminum3 commercial sol and commercial moisture to 2O- (Pt+K) pre dope gamma-aluminum 3 obtained powder, and carrying out wet grinding to it with a pot mill again. The amount relation between gamma-aluminum 2O3, and Pt and K is the phase which coated honeycomb support with the slurry and passed through baking eventually. When the amount of NOx occlusion catalyst support is 100 g/L (per honeycomb volume) It adjusted in the phase of mixed immersion so that Pt might serve as 30 g/cft (1.06 g/L) (weight of per honeycomb volume and Pt element base) and K might serve as 20 g/L (weight of per honeycomb volume and K element base). The addition of 2Oaluminum3 sol was made into the amount from which the solid content is 2Oaluminum3 conversion, and becomes 5% of the weight of all aluminum 2O3, and it was suitably added so that it might become the viscosity which a slurry tends to coat about moisture.
[0052] [Sample preparation]
(Example 1) Cordierite honeycomb support (septum thickness: 6mil (0.15mm), cel consistency:400cpsi (62 cels / cm2), 30% of porosity) was first immersed in 2Oaluminum3 commercial sol. Support was dried after blowing off the excessive liquid in a cel. The amount of support of 2Oaluminum3 sol was adjusted so that it might become 70 g/L (honeycomb support volume) after baking. When insufficient in the amount of support of the request by one-time immersion and desiccation, the process of immersion and desiccation was

repeated until it reached. The honeycomb object which is the obtained so-called primary alumina support support (only henceforth support support) was calcinated at 600 degrees C with the electric furnace for 1 hour. After baking, the process which coats this honeycomb object with the above-mentioned slurry for NOx occlusion catalyst coatings (it is hereafter called a "NOx occlusion catalyst slurry" for short), and is dried was repeated if needed until the amount of NOx occlusion catalyst support became 100 g/L. Then, it calcinated at 600 degrees C with the electric furnace again for 1 hour, and the NOx occlusion catalyst object 1 was acquired.
[0053] (Example 2) The amount of support of having made the baking conditions after supporting 2Oaluminum3 sol into 3 hours at 1200 degrees C, and 2Oaluminum3 sol NOx occlusion catalyst object 2(a) -2(c) was obtained like the example 1 except having adjusted so that it might become 70 g/L, 30 g/L, and 90 g/L (honeycomb support volume) after baking, respectively, and having manufactured the NOx occlusion catalyst object 2 (a), 2 (b), and 2 (c).
[0054] (Example 3) The NOx occlusion catalyst object 3 was acquired like the example 1 except having used the alumina support slurry A which are gamma alumina powder and the mixture of 1:1 of alumina sol instead of 2Oaluminum3 commercial sol. The amount of support of the slurry A for alumina support is the sum total of aluminum 2O3 originating in 2Ogamma-aluminum 3 powder in a slurry, and aluminum 2O3 originating in 2Oaluminum3 sol, and it was adjusted so that it might become 70 g/L after baking.
[0055] (Example 4) The NOx occlusion catalyst object 4 was acquired like the example 3 except having made the baking conditions after supporting the slurry A for alumina support into 3 hours at 1200 degrees C.

[0056] Instead of the slurry A for alumina support, the slurry B1 for alumina support is used for the NOx occlusion catalyst object 5 (a). (Example 5) Having manufactured baking conditions as 1 hour at 600 degrees C, and the NOx occlusion catalyst object 5 (b), The slurry B1 for alumina support, B-2, B3, and B4 were used for 5 (c), 5 (d), and 5 (e), respectively, and NOx occlusion catalyst object 5(a) -5(e) was obtained like the example 3 except having manufactured baking conditions as 3 hours at 1200 degrees C.
[0057] (The example of a comparison, and example of reference) The process which coats the same cordierite honeycomb support as having used in the example 1 with a NOx occlusion catalyst slurry, and is dried was repeated if needed until the amount of NOx occlusion catalyst support became 100 g/L. Then, it calcinated at 600 degrees C with the electric furnace for 1 hour, and the NOx occlusion catalyst object 6 was acquired.
[0058] (Example 6) The NOx occlusion catalyst object 7 was acquired like the example 1 except having repeated baking of 1 hour twice at 600 degrees C in the immersion to 2Oaluminum3 sol of cordierite honeycomb support, desiccation of support, and the electric furnace of a honeycomb object. The amount of support of 2Oaluminum3 sol was adjusted so that it might become a total of 70 g/L after two baking.
[0059] (Example 7) NOx occlusion catalyst object 8(a) -8(m) was obtained like the example 2 except having made it shown in a table 1 and a table 2 about the baking conditions in the immersion to cordierite honeycomb support, desiccation of support, and the electric furnace of a honeycomb object, and the amount of support.
[0060]
[A table 1]

触媒体No.	8(a)	8(b)	8(c)	8(d)	8(e)	8(f)	8(g)
ｺｰﾄ材の種類	ｱﾙﾐﾅｿﾞﾙ	ｱﾙﾐﾅｿﾞﾙ	ｱﾙﾐﾅｿﾞﾙ	αｱﾙﾐﾅ粉末+ｱﾙﾐﾅｿﾞﾙ	αｱﾙﾐﾅ粉末+ｱﾙﾐﾅｿﾞﾙ	αｱﾙﾐﾅ粉末+ﾑﾗｲﾄ粉末+ｱﾙﾐﾅｿﾞﾙ	ｱﾙﾐﾅｿﾞﾙ
混合比	-	-	-	1:1	1:1	0.5:0.5:1	-
第1回焼成条件	1200℃、3時間	600℃、1時間	1200℃、1時間	1200℃、3時間	-	1200℃、3時間	1200℃、3時間
ｺｰﾄ材の種類	ｱﾙﾐﾅｿﾞﾙ	ｱﾙﾐﾅｿﾞﾙ	ｱﾙﾐﾅｿﾞﾙ	ｱﾙﾐﾅｿﾞﾙ	ｱﾙﾐﾅｿﾞﾙ	ｱﾙﾐﾅｿﾞﾙ	γｱﾙﾐﾅ粉末+ｱﾙﾐﾅｿﾞﾙ
混合比	-	-	-	-	-	-	1:1
第2回焼成条件	1200℃、3時間	1200℃、3時間	600℃、1時間	600℃、1時間	600℃、1時間	600℃、1時間	600℃、1時間
ｱﾙﾐﾅ総担持量	70g/L	70g/L	70g/L	70g/L	70g/L	50g/L (ﾑﾗｲﾄ20g/L)	70g/L

[0061]
[A table 2]

触媒体No.	8(h)	8(i)	8(j)	8(k)	8(l)	8(m)
ｺｰﾄ材の種類	ｼﾘｶｿﾞﾙ	ｱﾙﾐﾅｿﾞﾙ	ｼﾘｶｿﾞﾙ	ｼﾘｶｿﾞﾙ	ｼﾘｶｿﾞﾙ+ｱﾙﾐﾅｿﾞﾙ	ｼﾘｶｿﾞﾙ+ｱﾙﾐﾅｿﾞﾙ
混合比	-	-	-	-	2:5	2:5
第1回焼成条件	600℃、1時間	1200℃、3時間	-	-	1200℃、3時間	1200℃、3時間
ｺｰﾄ材の種類	ｱﾙﾐﾅｿﾞﾙ	ｼﾘｶｿﾞﾙ	ｱﾙﾐﾅｿﾞﾙ	ｱﾙﾐﾅｿﾞﾙ	-	ｱﾙﾐﾅｿﾞﾙ
混合比	-	-	-	-	-	-
第2回焼成条件	600℃、1時間	600℃、1時間	600℃、1時間	1200℃、3時間	-	1200℃、3時間
ｱﾙﾐﾅ総担持量	30g/L (ｼﾘｶ40g/L)	30g/L (ｼﾘｶ40g/L)	30g/L (ｼﾘｶ40g/L)	30g/L (ｼﾘｶ40g/L)	50g/L (ｼﾘｶ20g/L)	60g/L (ｼﾘｶ10g/L)

[0062] [durability test] object [which was obtained as mentioned above / NOx occlusion catalyst] 1, 2, and 3 (a) - 3 (c), 4 and 5 (a) - 5 (e), and 6, 7 and 8 (a) - the acceleration durability test of 30 hours was presented with 8 (m) at 850 degrees C, making moisture live together 10% with an electric furnace. Moreover, the acceleration durability test was similarly presented with the cordierite honeycomb support which nothing supports as an example of reference.
[0063] [support degradation suppression effectiveness assessment] NOx occlusion catalyst object 1, 2, and 3 (a) - 3 (c), 4 and 5 (a) - 5 (e), and 6, 7 and 8 (a) - the existence of the crack initiation of the support after a durability test some was investigated by appearance observation and the microstructure observation by the electron microscope about the NOx occlusion catalyst object 6 which are 8 (m) and an example of a comparison. In addition, about the crack initiation situation, what generating of a crack was not accepted in at all was set to 0, and generating extent of a crack was evaluated in 11 steps as a thing 10 which a big crack which has a problem practically generated. Furthermore, comparison examination of the anti-chip box reinforcement after the first stage and a durability test was carried out. Those results are shown in a table 3.
[0064]
[A table 3]

実施例、比較例などの別	NOx吸蔵触媒体番号	クラック発生状況（耐久試験後）	抗折強度低下率（%）*
実施例1	1	4	34
実施例2	2（a）	3	25
実施例2	2（b）	6	46
実施例2	2（c）	3	23
実施例3	3	5	40
実施例4	4	4	32
実施例5	5（a）	4	36
実施例5	5（b）	3	31
実施例5	5（c）	6	51
実施例5	5（d）	5	38
実施例5	5（e）	8	66
実施例6	7	3	27
実施例7	8（a）	2	18
実施例7	8（b）	2	22
実施例7	8（c）	1	19
実施例7	8（d）	1	25
実施例7	8（e）	3	30
実施例7	8（f）	1	25
実施例7	8（g）	1	28
実施例7	8（h）	1	7
実施例7	8（i）	1	14
実施例7	8（j）	1	7
実施例7	8（k）	0	3
実施例7	8（l）	1	9
実施例7	8（m）	0	5
比較例	6	10	74
参考例	—	0	1

註：*

抗折強度低下率＝｛（初期強度－耐久試験後強度）／初期強度｝×１００（%）

[0065] NOx occlusion catalyst object 1, 2, and 3 (a) - based on [as shown in a table 3] this invention -- 3 (c), 4 and 5 (a) - 5 (e), and 7 and 8 (a) - the NOx occlusion catalyst object 6 (example of a comparison) with which no 8 (m) and (examples 1-7) contain an alumina shows that lowering on the strength was also small suppressed for the crack initiation of support by being stopped few. It was shown that there is an inclination for the NOx occlusion catalyst object which was more excellent from the above-mentioned result as compared with the case where the case where alumina sol is used uses alumina powder and alumina sol together when an alumina independent has been arranged to be acquired. Moreover, in the comparison between alumina powder, the inclination for what used the organic binder not to necessarily have enough effectiveness as compared with other things, and for the thing of alpha object to be superior to the thing of gamma object was accepted. About baking conditions, the result with the 2 times baking more desirable than 1-time baking was shown preferably [baking at 1200 degrees C which is an elevated temperature]. Furthermore, it became clear that the NOx occlusion catalyst object which was more excellent in combining and arranging a silica and an alumina was acquired.

[0066]

[Effect of the Invention] As opposed to the alkali metal and/or alkaline earth metal which use the catalyst object of this invention as a catalyst component as explained above a reactant low alumina Even if exposed to an elevated temperature by having arranged beforehand the alkali metal and/or alkaline earth metal which are used as a catalyst component by request, the matter which is easy to react, alkali alkali metal, and/or alkaline earth metal on the inside of support, and/or the cell wall front face of support Support is protected from the alkali metal and/or alkaline earth metal in catalyst material by the alumina, and the reaction with support is suppressed. Consequently, degradation of the support by alkali metal and/or alkaline earth metal is inhibited, and even if it carries the above catalyst material and uses it for a long period of time, the long-term activity of a catalyst object is attained.

[Translation done.]